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Improved Route to Bridged Planar Poly(*p*-phenylene) Derivatives for Maximization of Extended *p*-Conjugation

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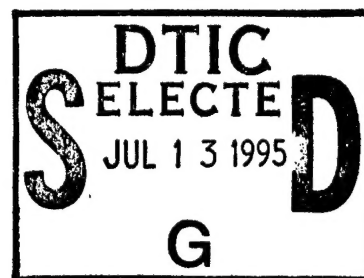
J. S. Lamba and J. M. Tour

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Department of Chemistry and Biochemistry
University of South Carolina
Columbia, SC 29208

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13. ABSTRACT (Maximum 200 words) Described will be an improved monomer synthesis for planar polyphenylene derivatives. A retrosynthetic approach is shown below. Both monomers come from a common arylbis(acid chloride).				
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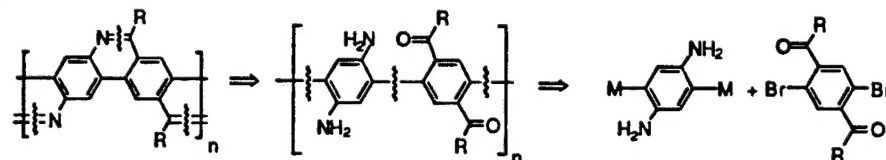
Improved Route to Bridged Planar Poly(*p*-phenylene) Derivatives for Maximization of Extended π -Conjugation

Jaydeep J. S. Lamba and James M. Tour*
 Department of Chemistry and Biochemistry
 University of South Carolina
 Columbia, South Carolina 29208

Poly(*p*-phenylene) (PPP), a highly insoluble polymer that has been studied extensively for its possible electronic and photonic applications, has a 23° twist between the consecutive aryl units due to ortho hydrogen interactions.¹ Attempts to enhance the solubility by substitution of the rings forces the consecutive aryl units even further out of plane resulting in a plummet of the extended conjugation (easily observed by the optical spectra).¹ We recently described a route to soluble ladder PPP derivatives.² Here we describe an improved synthetic route to the monomers as well as an aryl-substituted ladder PPP derivative.³

Our retrosynthetic approach involved two key steps (Scheme I, M = metal). First, imine cleavage to the

Scheme I

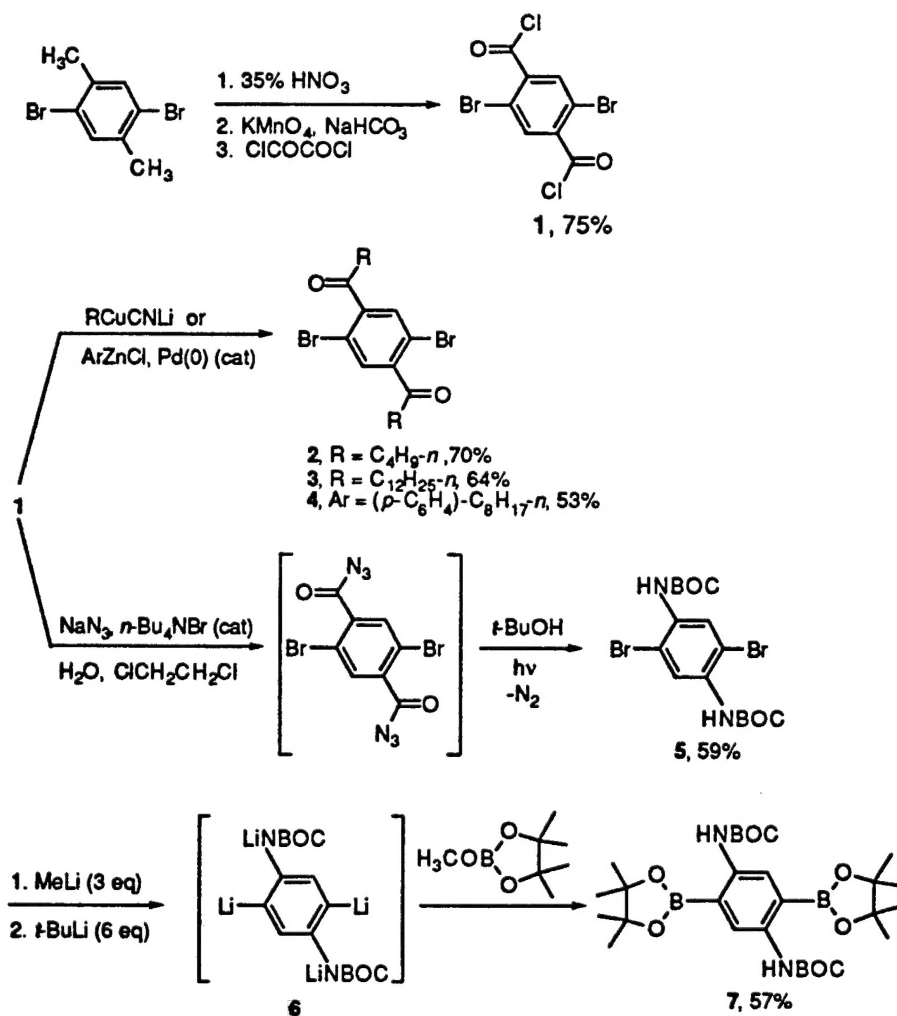


ketoamine functionalized PPP, and second, bond cleavage to the two arene systems shown. Since Pd(0)-catalyzed oxidative addition reactions are facilitated with electron deficient ring systems,⁴ we chose to keep the halides on the ketoaromatic portion.

After several nearly quantitative model reactions, we synthesized the two key monomers needed for the desired AB-type step growth polymerization. Dibromoxylene was oxidized by a two-step procedure⁵ which was superior to the one step Co(OAc)₂ procedure² described previously. The route described here is an improvement over our former approach in that the same dibromobis(acid chloride) (**1**) can be used for the synthesis of both the A and B monomer units. Conversion of **1** to the diketone was

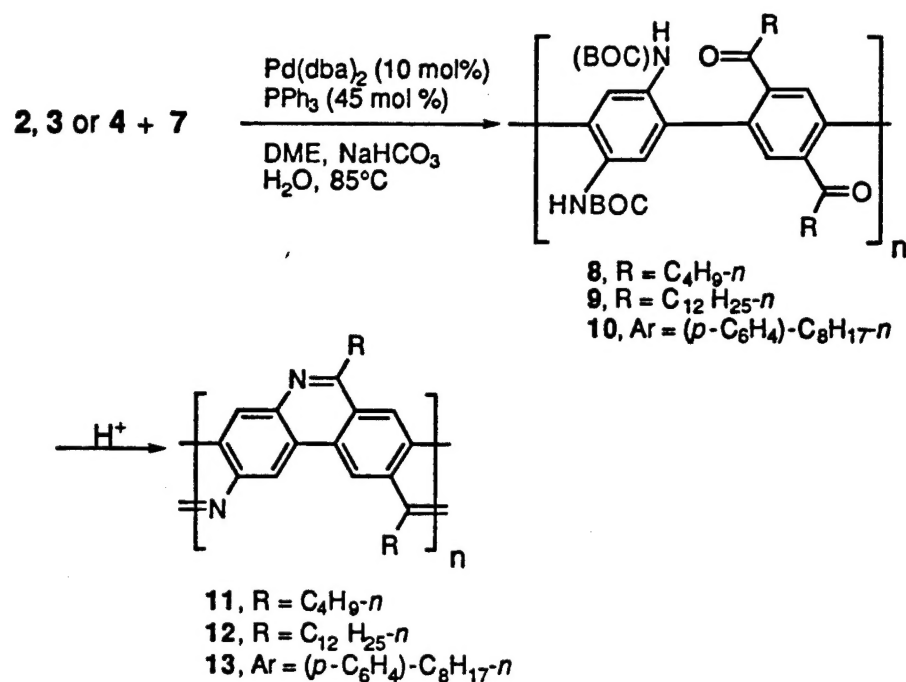
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accomplished with the use of the lower order alkylcyanocuprate, or an arylzinc halide and Pd(0) catalysis.⁶ This Pd(0)-catalyzed procedure proved to be superior for the aryl ketone formation. **1** could also be converted to the bis(acylazide) under phase transfer conditions. Photolysis with a UV TLC-spotting light affected the bis-Curtius rearrangement with N₂ expulsion. *t*-BuOH trapping of the bis(isocyanate) afforded the desired bis(BOC)-protected amine **5**.⁷ These phase transfer conditions and subsequent photochemical rearrangements were the only set of conditions that worked, in our studies, for this transformation. The yield of 59% for **5** is after repeated crystallization, thus, the efficiency of this process is quite good.



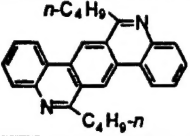
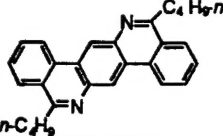
While **5** was nearly insoluble in ether at 0°C, it could be tetralithiated in ether to form a soluble intermediate **6** in almost quantitative yield (checked by addition of TMSCl and isolation of the arylbis(silane) after aqueous work-up). Treatment of **6** with methyl pinacol borate afforded the monomer **7** which could be purified by passage through a flash chromatography column containing a mixture of activated charcoal and Celite as the stationary phase (silica gel or neutral alumina caused rapid decomposition of the intermediate) and CH₂Cl₂ as the eluant followed by recrystallized to form pure **7**.

Reaction of **2**, **3**, or **4** with **7**, in the presence of a Pd(0) catalyst, yielded the soluble polymers **8**, **9**, and **10**, respectively, from which size exclusion chromatography (SEC) could be used to determine the hydrodynamic volumes relative to polystyrene (**8**: 63% yield after fractional precipitation, $M_n = 9,850$ with $M_w/M_n = 1.85$; **9**: 97% yield after fractional precipitation, $M_n = 28,400$ with $M_w/M_n = 3.70$; **10**: 80% yield after fractional precipitation, $M_n = 18,500$ with $M_w/M_n = 2.75$). Upon exposure of **8**, **9**, or **10** to trifluoroacetic acid (TFA), quantitative loss of the BOC protecting group and cyclization afforded **11** (90% yield), **12** (97% yield), and **13** (90% yield), respectively.⁸ All stretches for the ketone, carbamate, and amine in **8**, **9**, and **10** were absent in the FTIR spectrum of the planar polymers.



The optical absorption data showing enormous bathochromic shifts in the polymers upon cyclization (conversion of 8 to 11, 9 to 12, and 10 to 13); an observation consistent with the proposed ladder formation (Table I). The UV-vis spectrum of 13 in a CH₂Cl₂/trifluoroacetic acid (3/2) mixture is shown in Figure 1. The absorptions of these planar polymers are far more bathochromically-shifted than those of the planar trimers,⁹ oligo(*p*-phenylenes), and PPP.¹⁰

Table I. Optical Absorption Data

Compound	λ in solution (nm) ^a	λ of solid (nm) ^a
8	CH ₂ Cl ₂ : <u>250</u> , 306 (sh)	<u>248</u> , 308 ^b
9	CH ₂ Cl ₂ : <u>250</u> , 388	<u>250</u> , 398 ^b
10	CH ₂ Cl ₂ : <u>254</u>	<u>254</u>
11	CH ₂ Cl ₂ /TFA: 374, <u>396</u> , 426 (sh), 514, 520 (ed) ^c	-----
12	CH ₂ Cl ₂ /TFA: 376, <u>400</u> , 428, 478, 516, 530 (ed) ^c	<u>463-490</u> ^d
13	CH ₂ Cl ₂ /TFA: 380, <u>402</u> , 458, 506, 549 ^c	-----
	CH ₂ Cl ₂ : <u>300</u> (ref 9)	-----
	CH ₂ Cl ₂ : <u>294</u> (ref 9)	-----
<i>p</i> -sexiphenylene	CHCl ₃ : <u>318</u> (ref 10)	-----
PPP (calcd infinite <i>M_n</i>)	<u>344</u> (ref 10)	-----

^a λ_{\max} is underlined, (sh) is shoulder, (ed) is tailing edge at ~10% of λ_{\max} intensity. ^bAlso a strong carbonyl absorption at 196 nm. ^cSpectrum recorded on the acid solubilized, therefore, multiprotonated system. ^dThese λ_{\max} values were recorded on a series of four different polymer samples of 9 in order to insure their reproducibility.¹¹

Figure 1. UV-vis spectrum of 13 in a CH₂Cl₂/TFA (3/2) mixture

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- (8) 8: Anal. calc'd for $(C_{32}H_{42}N_2O_6)_n$: C, 69.79; H, 7.69; N, 5.07. Found: C, 70.55; H, 7.25; Br, <0.5; N, 5.13. 9: Anal. calc'd for $(C_{48}H_{74}N_2O_6)_n$: C, 74.38; H, 9.62; N, 3.61. Found: C, 74.99; H, 9.40; Br, <0.5; N, 3.55. 11: Anal. calc'd for $(C_{22}H_{22}N_2)_n$: C, 84.04; H, 7.05; N, 8.91. Found: C, 79.13; H, 6.77; Br, <0.5; N, 8.56. 12: Anal. calc'd for $(C_{38}H_{54}N_2)_n$: C, 84.70; H, 10.10; N, 5.20. Found: C, 81.45; H, 9.64; Br, <0.5; N, 5.22.
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- (11) Drs. R. Gaudiana and P. Mehta of Polaroid Corporation kindly provided the solid-state UV-vis data.

